Synthesis and Properties of New Platinum Complexes with 2-Phenylimidazo[1,2-a]pyridine Ligands

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1. Introduction
Phosphorescent Pt(II) complexes have attracted much attention owing to their potential applications in OLEDs [1]. However, the Pt complexes showing efficient EL properties have not been fully developed compared to Ir(III) complexes. Particularly, blue-emitive Pt complexes have been less explored. The square-planar structures often cause π-π interactions, leading to longer wavelength emission and less efficiency [2]. On the other hand, single dopant white OLEDs are possible using well-balanced monomer and aggregate states [3]. We have recently developed new color tunable Ir(III) complexes with 2-phenylimidazo[1,2-a]pyridine (PIP) ligands [4]. One of advantages of the PIP ligands is that substituents can be easily introduced into the PIP skeleton to tune the emission-color. We have succeeded in preparing blue-emitted Ir complexes. The PIP ligands have now been applied to Pt complexes to achieve blue emission. We have prepared new Pt complexes 1–4. Flouorines were introduced on the phenyl ring to lower the HOMO levels and obtain blue-shifted phosphorescence. In addition, phenyl and 3,5-dimethylphenyl groups were introduced on the imidazole ring to control π-π interactions in the solid state by the twisted phenyl groups. In this paper their synthesis, structures, electrochemical and photophysical properties in solution and the solid state are reported. Particularly, to clarify the π-π interactions in the solid state, the relationship between the solid state luminescence and crystal structure was investigated in detail by X-ray structure analysis.

2. Method
2.1 Materials
2-Phenylimidazo[1,2-a]pyridines were prepared by modification of the reported methods. The phenyl groups were introduced by using the Suzuki coupling reactions. Pt complexes 1–4 with acetylacetonate (acac) as an ancillary ligand were prepared by a two-step reaction via Pt(II)-μ-chloro-bridged dimer complexes [5] in 14–19% over all yields.

2.2 Electrochemical measurements
Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out using BAS 100B system. Anhydrous DMF was used as solvent under argon, and 0.1 M tetra(n-butyl)ammonium hexafluorophosphate was used as supporting electrolyte. Pt disk, Pt wire and SCE were used as working, counter and reference electrodes, respectively.

2.3 X-ray crystallography
Reflection data were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with Mo-Kα radiation (λ = 0.71075 Å) at 93 K. Absorption collection for these data was applied using empirical or numerical procedures. All the structures were solved by heavy-atom Patterson methods and refined by full matrix least-squares on

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F² with TEXSAN.

3. Results and Discussion

The Pt complexes 1-4 show both oxidation and reduction potentials. The oxidation potentials of 1-4 were observed at +0.66, +0.81, +0.77, +0.85 V, respectively. The values become higher by the introduction of fluorines, indicating that the HOMO levels are decreased. The reduction potentials of 1-4 were also observed at -2.65, -2.57, -2.57, -2.53 V, respectively, indicating that the LUMOs were also affected by the fluorine groups and the introduction of the phenyl group to the imidazole ring has no effect on the LUMOs. This result was supported by the AM1 calculations of the complex 1, showing that the HOMO consists of a mixture of phenyl, imidazole-π (3-position) and Pt orbitals, while the LUMO lies predominantly on the pyridine ring of the imidazol[1,2-a]pyridine.

Single crystals of Pt complexes 2-4 were obtained by recrystallization although the single crystals of 1 could not be obtained. The X-ray crystal structure analysis of complexes 2-4 was carried out. In all of the complexes, the platinum center exhibits square planar coordination, and the Pt(P)IP(acac) parts are almost planar. The Pt-C, Pt-N, Pt-O bondlengths are identical in the three complexes, indicating that the phenyl groups of the imidazole ring have no influence on the bondlengths. In the complexes 3 and 4, the phenyl rings tilt ca. 50° from the imidazole ring owing to the steric hindrance. The molecules of 2-4 pack as head-to-tail dimer and each molecule of the dimer is related to the other by a center of inversion. The intermolecular distances in the dimers are 3.31 Å for 2, 3.36 Å for 3 and 3.46 Å for 4, which are short enough for π-π interactions. No Pt-Pt short contacts are not observed in them. An important feature is that the complex 2 dimerizes with overlapping over the whole phenylimidazopyridine plane, whereas the complex of 3 having a phenyl group dimerizes only with the imidazopyridine part. In the complex 4 with a 3,5-dimethylphenyl group, the intermolecular π-π interaction is further restricted. This finding can be attributed to the steric hindrance of the phenyl groups on the imidazole ring. The interplanar distance is increased with an increase of the degree of the steric interaction.

The PL properties of the Pt complexes under various conditions are summarized in Table 1. Non-substituted complex 1 exhibited blue phosphorescence at low temperature. The emission maxima of 2 is more blue-shifted by ca. 4 nm than those of 1. This is consistent with the consideration of the HOMO, LUMO levels, where the HOMO is more effectively lowered by the introduction of fluorines. On the other hand, complexes 3 and 4 showed identical emission maxima, which are a little red-shifted from those of 1.

Table 1. Emission maxima of Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>77 K a</th>
<th>298 K b</th>
<th>Solid state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>471; 507; 546</td>
<td>481; 515</td>
<td>492; 531, 582, 623</td>
</tr>
<tr>
<td>2</td>
<td>467; 502; 542</td>
<td>476; 512</td>
<td>483; 556</td>
</tr>
<tr>
<td>3</td>
<td>475; 511; 550</td>
<td>485; 520</td>
<td>485; 523</td>
</tr>
<tr>
<td>4</td>
<td>475; 511; 550</td>
<td>486; 524</td>
<td>486; 524</td>
</tr>
</tbody>
</table>

a In 2-MeTHF. b In CH₂Cl₂.

Although all the complexes showed phosphorescence in solution at room temperature, the quantum efficiencies were low. The quantum yield of 1 was 1.5%. The emission maxima at room temperature are red-shifted by ca. 10 nm in all the complexes. Interestingly, in the solid PL spectra of 1 and 2, new peaks appeared although complexes 3 and 4 showed the similar spectra between the solution and solid. In particular, complex 2 showed strong emission at 556 nm, whose intensity is about 6 times as that at 483 nm. The low-energy emissions observed in 1 and 2 can be attributed to the excimer formation originating from efficient π-π stacking interaction in the solid state. X-ray crystal analysis has demonstrated that the phenyl groups prevent such intermolecular interactions as described before. This explanation is also rationalized by the fact that the 0-0 bands of 1 and 2 in the solid are red-shifted by 11 and 7 nm from in solution, whereas no shifts were observed in 3 and 4. These results confirm that the readily introduced phenyl groups on the imidazole ring in PIP-based Pt complexes effectively prevent the bathochromic shifts and the low-energy emissions caused by π-π interactions in the solid state.

References